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COMPLETE SPECIFICATION.

A Process for Obtaining Partly Hydrolysed Polvinyl Ester.

We, MINISTERUL INDUSTRIEI PETROLULUI SI CHIMIEI, of strada Scaune 1, Bucharest, Roumania, a Roumanian Corporation, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present specification relates to a process for obtaining partly hydrolysed polyvinyl ester, for instance for use as a protective colloid in emulsion polymerisation processes. The best protective colloid for this purpose is considered to be a partly hydrolysed polyvinyl ester with a degree of hydrolysis of $83\pm2\%$, or a saponification number of $110\pm1/10$ mg KOH/g.

Polyvinyl alcohol is generally obtained by the acid or alkaline saponification of polyvinyl acetate. In the case of alkaline saponification, processes using an alkali metal hydroxide and catalytic processes using sodium methylate are distinguished. The process of saponification with sodium methylate is carried out as follows:

A mixer is charged with 100 kg. of polyvinyl acetate obtained by suspension polymerisation, which is dissolved in 120 l. of methanol at a temperature of 60° C. After 5 to 6 hours of homogenisation the solution is cooled for 4 to 5 hours to a temperature of 20° C. Sodium methylate is then introduced in proportion. The addition of the methylate takes 5 to 6 hours. Samples are taken from time to time from which the saponification number is determined. When a value of 180 ± 20 is reached, the mixer is heated for 3 to 4 hours and the solvent is recovered. During recovery the saponification reaction continues and the saponification number obtained depends on the conditions of recovery. The treatment of a charge according to the process described above takes 20 to 30 hours.

The disadvantages of this process are its long duration owing to the heating and cooling operations and the uncertainty of the saponification number finally obtained because of the recovery phase and due to the slow checking of saponification owing to the fact that determinations of the saponification number are effected, this analysis taking 1 to 2 hours.

In view of the fact that saponification is conducted at a temperature of 20° C., the viscosity of the mixture in the mixer reaches the threshold of the precipitation of the values resulting in over-actuation of the stirring system.

According to the present invention, there is provided a process for the production of partly hydrolysed polyvinyl ester of a predetermined degree of hydrolysis by alkaline (alkali metal) saponification of polyvinyl ester of a carboxylic acid in a liquid medium, including treating the polyvinyl ester in the presence of water with a material providing alkali metal ions after predetermining the ratio between the alkali metal and the water to predetermine the degree of hydrolysis of the polyvinyl ester, and allowing the saponification to continue until it ceases spontaneously.

The saponification process can be checked by rapid colorimetric analysis based on the colour reaction of polyvinyl alcohol with a solution of iodine and boric acid.

After saponification has ceased spontaneously at the desired number, a quantity of water or dilute solution of acetic acid can be added to ensure that the reaction has ceased in the recovery phase itself.

For example, a cold mixer is charged with 100 kg of polyvinyl acetate suspension, the stirring system is stopped to grind the agglomerations of beads and 100 to 150 kg

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of methanol and 20 to 50 kg of methyl acetate are introduced. The contents of the mixer are heated to 54 to 60° C. and stirring is continued until the mixture is completely homogenised. Meanwhile the water content of the material introduced is determined. A quantity of sodium in the form of methylate is added according to the water content determined, so that the ratio between the percentages of sodium and of water is 0.160 to 0.165. The progress of saponification is checked by dissolving dried samples weighing about 0.3 g in 20 ml of water, adding two drops of n/10 iodine solution and 5 ml of a saturated solution of boric acid. The concentration obtained is compared with a standard scale. 1 to 2 hours after the introduction of the methylate, the reaction ceases spontaneously, a polyvinyl ester with a saponification number of 110 ± 10 being obtained. The saponification number is checked, after which 5 l. of water or 300 ml of acetic acid diluted to 5 l. with distilled water are introduced. The solvent is recovered. The treatment of a charge takes 8 to 12 hours.

The process according to the invention has the following advantages:

The operations of heating and cooling the mixer can be dispensed with;

The period required for the treatment of a charge can be shortened from 20 to 30 hours to 8 to 12 hours, which increases the productivity of the installation;

The obtaining of a saponification number of 110 ± 10 can be ensured;

The saponification number can be checked while saponification is in progress, and

As the operation is carried out at a temperature of 54 to 60° C., the stirring system need not be over-actuated.

WHAT WE CLAIM IS:—

1. A process for the production of partly hydrolysed polyvinyl ester of a predetermined degree of hydrolysis by alkaline (alkali metal) saponification of polyvinyl ester of a carboxylic acid in a liquid medium, including treating the polyvinyl ester in the presence of water with a material providing alkali metal ions after predetermining the ratio between the alkali metal and the water to predetermine the degree of hydrolysis of the polyvinyl ester, and allowing the saponification to continue until it ceases spontaneously.

2. A process as claimed in claim 1, wherein the saponification is effected at a temperature above room temperature.

3. A process as claimed in claim 2, wherein the saponification is effected at a temperature above 50° C.

4. A process as claimed in claim 3, wherein the saponification is effected at a constant temperature of 54°—60° C.

5. A process as claimed in any one of the preceding claims, wherein the alkali metal is sodium.

6. A process as claimed in claim 5, wherein the weight ratio of sodium : water is from 0.160 : 1 to 0.165 : 1, the product having a saponification number of 110 ± 10.

7. A process as claimed in any one of the preceding claims wherein the polyvinyl ester is polyvinyl acetate.

8. A process as claimed in any one of the preceding claims, wherein the alkali metal is added as an alkali metal alkoxide.

9. A process as claimed in claim 8, wherein the alkali metal alkoxide is the alkali metal methylate.

10. A process as claimed in any one of the preceding claims, wherein the liquid medium is methanol.

11. A process as claimed in any one of the preceding claims, wherein the degree of hydrolysis during the saponification is determined during the treatment.

12. A process as claimed in claim 11, wherein the degree of hydrolysis during the saponification is determined during the treatment by testing samples by colorimetric analysis.

13. A process as claimed in claim 12, wherein each sample is dissolved in water, and iodine and boric acid are added, the colour concentration being compared with a standard scale.

14. A process as claimed in claim 13, wherein the sample is dried, 0.3 gms. of each sample is dissolved in 20 ml. of water, and two drops N/10 iodine solution and 5 ml. of saturated boric acid solution are added, or corresponding proportions for a sample of a different weight.

15. A process as claimed in any one of the preceding claims, wherein, after the saponification has ceased spontaneously, the degree of hydrolysis is fixed for the recovery stage by adding water or aqueous acetic acid.

16. A process as claimed in claim 1, and substantially as hereinbefore described.

17. Partly hydrolysed polyvinyl ester which has been produced by a process as claimed in any one of the preceding claims.

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